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(54) **Process for the carbonylation of olefins.**

(57) A process for the carbonylation of an olefin with carbon monoxide in the presence of water, an alcohol, and/or a carboxylic acid, the reaction being conducted in the presence of an essentially halide-free palladium catalyst and a tri-organophosphine and in the absence of sodium acetate, the tri-organophosphine containing at least one aliphatic carbon atom bound to phosphorus and the molar ratio of the organophosphine to palladium being less than 10:1.

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PROCESS FOR THE CARBONYLATION OF OLEFINS

This invention relates to a process for the carbonylation of olefins.

Many processes have been described in which olefins are carbonylated in the presence of water, alcohols or
5 carboxylic acids to produce carboxylic acids, esters or anhydrides, respectively. For example, US 3168553 discloses that carbonylation can be effected by the use of a complex catalyst comprising cobalt, ruthenium, rhodium or iridium together with a tri-organophosphine. However,
10 in this process, extremely high pressures are required, and complex mixtures of products are formed. For example when using the preferred catalyst, $\text{Co}_2(\text{CO})_8$, in the reaction of ethanol with ethylene, the yield of the desired product, ethyl propionate, is always very much
15 less than the yield of other products.

US 3917677 discloses that the use of halogen-free rhodium catalysts in the presence of tri-organophosphines can be used to produce esters by the carbonylation of olefins in the presence of alcohols. Using this system,
20 relatively high yields of ester are formed, but when using alkenes having 3 or more carbon atoms, the relative amounts of terminal and internal esters are similar, with the internal esters usually predominating. The best ratio of terminal:internal ester obtained is
25 60:40. This specification also provides comparative data which indicate that the replacement of the rhodium catalyst by palladium produces no carbonylation reaction at all.

Attempts to use palladium catalysts, which are
30 rather cheaper than rhodium catalysts, have been made. German Offenlegungsschrift No. 2410246 discloses that if a zero-valent palladium tri-organophosphine complex

is used as catalyst in the presence of a large excess of tri-organophosphine. carbonylation reactions will occur. However. relatively high pressures are required. the cost of the excess phosphine is high, and the process is not entirely satisfactory when olefins having internal double bonds are used as feedstock.

US specification 3437676 also describes the use of specific palladium catalysts. The Examples in this US specification show that the proportion of terminal product as opposed to internal product is generally very low, and that very high pressures are required to ensure efficient reaction.

It has now been found that by the selection of very specific catalyst components. many of the disadvantages of the prior art can be overcome.

The invention therefore provides a process for the carbonylation of an olefin with carbon monoxide in the presence of water, an alcohol, and/or a carboxylic acid, characterized by conducting the reaction in the presence of an essentially halide-free palladium catalyst and a tri-organophosphine and in the absence of sodium acetate. the tri-organophosphine containing at least one aliphatic carbon atom bound to phosphorus and the molar ratio of the organophosphine to palladium being less than 10:1.

A wide range of olefins can be carbonylated using the process according to the invention. for example those having from 2 to 30. especially 2 to 20. carbon atoms. The olefin may be an unsubstituted alkene. or it may contain one or more substituents. Inert substituents which may be present include halogen atoms and cyano. ester, alkoxy and aryl groups. In addition. the olefin may contain one or more substituents which are not inert under the reaction conditions. for example hydroxy or carboxy groups. The fate of such groups will depend on the precise reaction conditions: for example.

a carboxy substituted olefin may be carbonylated in the presence of an alcohol. in which case the main products are compounds in which the acid group has been converted into an ester group by reaction with the alcohol. Alternatively, under some reaction conditions, the carboxy group may actually take part in the carbonylation of the olefin function of a second molecule of olefinic acid. One or more double bonds may be present in any position in the olefin carbon chain. Unsubstituted alkenes with one or two double bonds are preferred, and straight-chain alkenes are especially preferred. A mixture of different olefins can of course be used.

Carbonylation reactions using olefins with more than two carbon atoms in the alkene chain can of course lead to a variety of products. For example, the reaction of propene with water could lead to propane-1-carboxylic acid or to propane-2-carboxylic acid. It is an advantage of the present invention that when using an olefin with more than two carbon atoms in the alkene chain, a high proportion of the product usually contains a terminal carbonyl group, regardless of the position of the double bond(s) in the starting material.

A wide range of alcohols and carboxylic acids may be used as reactant in the process of the invention. For example, the compound may be aliphatic, cycloaliphatic or aromatic, and may carry one or more inert substituents, for example those described above for the olefinic reactant. The compound suitably contains up to 20 carbon atoms. One or more hydroxy and/or carboxy groups may be present, in which case different products can be obtained as desired depending upon the molar ratio of reactants used. For example, a trihydric alcohol can be reacted with a small quantity of olefin to produce a mono-ester. or with a large quantity of olefin to produce a tri-ester.

Thus the choice of hydroxylic compound depends solely on the desired product. The use of water produces carboxylic acids as the initial product. The use of alcohols produces esters, and these can of course be poly-esters as described above. Alkanols such as methanol, ethanol, propanol or trimethylolpropane, and alcohols containing ether linkages, for example triethylene glycol, all produce useful products. The use of carboxylic acids produces acid anhydrides. If an alkanolic acid having $n+1$ carbon atoms is reacted with an alkene having n carbon atoms, a symmetrical anhydride is produced. Otherwise a mixed anhydride is initially produced.

However, depending on the reaction conditions, further reactions may take place. For example, if an olefin is reacted with water and carbon monoxide, the carboxylic acid produced may react with more olefin and carbon monoxide to produce an anhydride. An ester produced may be hydrolyzed if water is present in the reaction mixture, to form an acid and an alcohol, which may in turn react with further olefin. Similarly, an anhydride may be hydrolysed to form an acid or acids. Thus careful control of the process according to the invention means that a wide range of products can be produced as desired.

If it is desired to prepare a particular acid by the process according to the invention, it may for example be convenient to react one mole of said acid with the corresponding olefin having one less carbon atom to produce the symmetric anhydride; to hydrolyse this anhydride to produce two moles of acid; and to recycle one mole of said acid back to the first stage of the process.

When an alcohol is used as the main hydroxylic reactant in the process of the invention, it has, surprisingly, been found that the addition of small quan-

titles of water and/or an acid, especially a carboxylic acid, to the reaction mixture has a strongly promoting effect on the rate of the reaction of the olefin with the alcohol. Suitable carboxylic acids include alkanolic acids having up to 12 carbon atoms. The water and/or acid is suitably added in an amount of from 1 to 5 mole percent based upon the number of moles of olefin. Hydrohalic acids should preferably not be added to the reaction mixture as they are a source of free halogen and have a detrimental effect upon the reaction, as described below. A similar promoting effect is obtained by the addition of water to a system in which an acid is the principle reactant, and by the addition of an acid to a system in which water is the principle reactant.

The palladium catalyst used in the process according to the invention may be homogeneous, heterogeneous, or partially homogeneous and partially heterogeneous, and should be essentially free from halide ions. Suitable homogeneous catalyst components include salts of palladium with mineral acids other than hydrohalic acids, for example nitrates, sulphates or perchlorates, or with organic acids, for example alkanolic acids having up to 12 carbon atoms. Palladium acetate is an especially suitable homogeneous catalyst. Heterogeneous catalysts comprise metallic palladium or palladium salts deposited on an inert carrier material, for example palladium charcoal. Generally the use of a homogeneous catalyst is preferred, since such catalysts tend to be rather more active than heterogeneous catalysts. However, when using as reactant a long-chain olefin, for example one having more than 6 carbon atoms, and having an internal rather than a terminal double bond, the proportion of product having a terminal carbonyl group tends to be greater when using a heterogeneous catalyst. This catalyst may be used alone under such conditions, but is

preferably used in admixture with a homogeneous catalyst which tends to increase the rate of the reaction.

The amount of palladium catalyst used is not critical. Generally from about 0.0001 to 10 moles of palladium are used per mole of olefinic double bond to be carbonylated, the preferred range being from 0.01 to 5 moles per mole.

It may be desirable to add a co-catalyst to the system. It has been found that the use of a cobalt-containing catalyst in conjunction with the palladium catalyst is advantageous, particularly for the preparation of terminally functionalised compounds from olefins having an internal double bond.

The tri-organophosphine promotor used in the process according to the invention must have at least one aliphatic carbon atom bonded to phosphorus. Suitable phosphines include those of the general formula



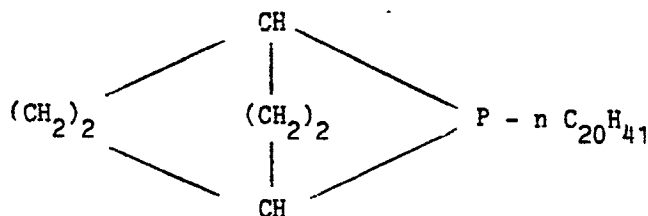
in which each of R^1 and R^2 independently represents an optionally substituted alkyl, cycloalkyl or aryl group, or together represent an optionally substituted alkylene group, and R^3 represents an optionally substituted alkyl or cycloalkyl group. Preferably any alkyl group has up to 20 carbon atoms, any cycloalkyl group preferably has from 5 to 7 carbon atoms, and any aryl group preferably has up to 18 carbon atoms; phenyl groups are preferred aryl groups. Preferably an alkylene group has from 4 to 9, especially 6 to 8, carbon atoms, and such a group may form a monocyclic or a bicyclic ring containing the phosphorus atom.

Possible optional substituents include those given above for the olefinic reactant. Preferably however R^1 , R^2 and R^3 are hydrocarbon groups. Preferably R^3 is an

unsubstituted alkyl or cycloalkyl group, an alkyl group substituted by a phenyl group, or an alkyl group substituted by a group $-PR^1R^2$ where R^1 and R^2 have the above meanings. Typical groups R^3 include methyl, ethyl, propyl, isopropyl, butyl, lauryl, cyclopentyl, cyclohexyl, benzyl, 2-phenylethyl and $-\text{CH}_2-\text{P}(\text{phenyl})_2$.

Especially preferred phosphines are those of formula I in which at least one and preferably both of R^1 and R^2 are bound to the phosphorus atom by an aliphatic carbon atom. For example, R^1 and R^2 may have one of the preferred meanings given above for R^3 . For economic reasons, it may be preferred to use a phosphine in which all of R^1 , R^2 and R^3 represent the same group, especially an unsubstituted alkyl group.

Thus typical phosphines include trimethylphosphine, triethylphosphine, tributylphosphine, $(\text{phenyl})_2\text{P}-\text{CH}_2-\text{P}(\text{phenyl})_2$ and cyclic structures such as:



The molar ratio of the tri-organophosphine to palladium (calculated as atomic palladium) must be less than 10:1, and is preferably in the range of from 2:1 to 6:1.

The carbon monoxide required for the reaction may be supplied in substantially pure form, or diluted with any inert gas, for example nitrogen. The presence of more than minor amounts of hydrogen in the gas stream is undesirable since hydrogenation of the olefin then takes place under the reaction conditions. Generally it is preferred that the amount of hydrogen in the gas stream should be less than 5% by volume.

The process according to the invention is carried out using an essentially halide-free palladium catalyst, and preferably the reaction system as a whole is substantially free from halide, and from compounds which generate halide under the reaction conditions. The presence of halide in commercial plants is most undesirable because of the highly corrosive nature of halide. Moreover, the presence of halide ions exerts an inhibiting effect on the process according to the present invention, and is thus not to be recommended.

US patent Specification No. 3917677, which claims the use of rhodium catalysts in the carbonylation of olefins, provides comparative data which show that the carbonylation of ethylene in the presence of methanol, tributylphosphine, sodium acetate (as a buffer) and either $\text{Pd}(\text{triphenylphosphine})_3\text{Cl}_2$ or palladium acetate, gives no reaction at all. This is attributed to the inactivity of the palladium catalyst. Thus the activity of the specific sodium acetate free palladium catalyst systems used in the process of the present invention is contrary to expectation. The reason for the inhibiting effect of sodium acetate in the prior art process is not understood. However, without being bound by any particular theory, it is believed that the presence of the sodium acetate, a buffer, leads to basic species under the reaction conditions. As stated above, the present process is promoted by the presence of acid. It is therefore believed to be desirable that basic compounds should not be present in the reaction mixture.

The process according to the invention permits the use of very mild reaction conditions. Temperatures in the range of from 100 to 200°C, especially 120 to 150°C, are generally suitable. The pressure may vary over a wide range. Generally, a pressure in the range of from 25 to 100 atmospheres gauge is suitable, with pressures

of from 30 to 60 atmospheres gauge being preferred. Higher pressures may of course be used. but are usually economically unattractive.

The molar ratio of the reactants is not critical. and generally the molar ratio of hydroxy groups to olefinic bonds may be in the range of from 0.1:1 to 10:1. When using a mono-olefin and either water, a mono-hydric alcohol or a mono-basic acid, it is usually preferred to use an excess of the hydroxy compound, but as discussed above. if using a poly-hydric alcohol or a poly-basic acid to prepare a poly-ester or a poly-anhydride, it is usually necessary to use an excess of the olefin.

A separate solvent is not essential in the process according to the invention. and often a large excess of one of the reactants, usually the hydroxylic reactant, may form a convenient reaction medium. However, it may in some cases be desirable to use a separate solvent. and any suitable inert medium may be used. A suitable solvent may for example be selected from sulphoxides and sulphones, for example dimethylsulphoxide, diisopropylsulphone or sulfolane, ketones. for example acetone or methyl isobutyl ketone, and ethers. for example diisopropylether. It is often convenient to use as solvent the compound which is the initial reaction product of the carbonylation reaction.

The following Examples illustrate the invention. Unless otherwise specifically stated, all the experiments were carried out in the following manner. A 300 ml magnet-driven autoclave of Hastelloy C (Trade Mark) was charged with 50 ml methanol and the other stated liquid and solid components of the reaction mixture, flushed with carbon monoxide, and then pressurized with further carbon monoxide and any other stated gaseous component. The autoclave was then heated to a temperature of 135°C. and maintained at that temperature for 15 hours. After

this time the contents of the autoclave were analysed by gas-liquid chromatography.

Example 1

5 The autoclave was charged with 0.7 mmol palladium acetate and 4 mmol tri-n-butylphosphine, and pressurized with 20 bar ethene and 20 bar CO. 34% by weight of the resulting reaction mixture was methyl propionate. the only significant by-product being 0.2% by weight of methyl acetate.

10 Example 2 (comparison)

Example 1 was repeated exactly except that the tri-n-butylphosphine was replaced with 4 mmol triphenylphosphine. The reaction mixture contained only 5% by weight of methyl propionate.

15 Examples 3 to 8

The olefin used was propene at a pressure of 8 bar. and CO was added at a pressure of 30 bar. The results obtained are tabulated below. The components present in the system are given in units of mmol unless otherwise
20 stated, and the ester production rate is in units of ester produced per gram palladium (calculated as atomic palladium) per hour.

Example No.	Components Present (mmol)	Ester production rate (g/gPd/h)	% terminal ester
3	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃	3	73
4	1.4 Pd(CH ₃ CO ₂) ₂ 4/(phenyl) ₂ P/2CH ₂	5	80
5	0.7 Pd(CH ₃ CO ₂) ₂ 4 eicosyl phosphabicyclononane	4	80
6	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 40 CH ₃ CO ₂ H	11	75
7	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 150 H ₂ O	12	75
8	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 10 g dimethylsulphone	5	80

In all these examples, the products were exclusively esters of C₄ acids, with no detectable side-products being obtained.

The results of Examples 6 and 7 show that the addition of water or acetic acid to the reaction mixture increases the rate of production of ester considerably without having any marked detrimental effect on selectivity.

Example 9 (comparison)

The procedure of Example 3 was repeated exactly except that an amount of 880 mg sodium acetate was added to the reaction mixture. No reaction at all took place, as expected from the result of Example 5 of US Patent 3917677.

Examples 10 to 12

10 ml of C₅ olefin were used as reactant, with a

CO pressure of 30 bar. The results are tabulated below.
The only products obtained were esters.

Example No.	Components present.	Olefin	Ester pro- duction rate.	Terminal ester.
	mmol		g/g Pd/h	%
10	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 150 H ₂ O	pentene-1	10	79
11	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 150 H ₂ O	pentene-2	2.5	70
12	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 150 H ₂ O 0.35 Co ₂ (CO) ₈	pentene-2	7	72

Examples 13 and 14

The olefin reactant was 10 ml cis hexene-3. and CO pressure was 30 bar. The results are tabulated below.

Example No.	Components present.	Ester production rate.	Terminal ester.
	mmol	g/g Pd/h	%
13	0.7Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 150 water	2	72
14	0.7 Pd(CH ₃ CO ₂) ₂ 4 P(nBu) ₃ 40 CH ₃ CO ₂ H	5	75

Example 15

Example 13 was repeated except that the water was replaced by 10% HCl solution. Only 43% of the product obtained was terminal ester, illustrating that the pre-

sence of halide has a marked effect upon the reaction.

Example 16

The catalyst used was 0.7 mmol palladium acetate and 4 mmol tri-n-butylphosphine. the olefin used was
5 10 ml octene-1. and a CO pressure of 20 bar was used. The selectivity to methyl esters of C₉ acids was 100%, the ester production rate was 3 g/gPd/h, and the ester product contained 70% of terminal ester.

Example 17 to 22

10 A series of experiments were carried out using C₁₂ mono-olefins with either a terminal or an internal double bond. 10 ml olefin were used in each case. the CO pressure being 30 bar. Example 17 was carried out using only 25 ml methanol instead of 50 ml. The re-
15 sults are tabulated below.

Example No.	Components present. mmol	Olefin double bond position	Conversion of olefin to ester. %	Terminal ester. %
17	0.7 $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ 4 $\text{P}(\text{nBu})_3$ 150 H_2O 25 ml sulpholane	terminal	31	71
18	0.7 $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ 4 $\text{P}(\text{nBu})_3$ 50 $\text{CH}_3\text{CO}_2\text{H}$	terminal	54	69
19	0.7 $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ 4 $\text{P}(\text{nBu})_3$ 50 octanoic acid 0.5 g of 3%w palladium on charcoal	terminal	70	74
20	4 $\text{P}(\text{nBu})_3$ 50 $\text{CH}_3\text{CO}_2\text{H}$ 0.2 g of 10%w palladium on charcoal	terminal	46	75
21	0.7 $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ 4 $\text{P}(\text{nBu})_3$ 50 $\text{CH}_3\text{CO}_2\text{H}$ 0.5 g of 3%w palladium on charcoal	terminal	64	73
22	0.7 $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ 4 $\text{P}(\text{nBu})_3$ 50 $\text{CH}_3\text{CO}_2\text{H}$ 0.5 g of 3%w palladium on charcoal	internal	26	68

Example 23

Example 18 was repeated using a higher CO pressure of 50 bar. The conversion increased from 54 to 65% and the percentage of terminal ester in the product increased from 69 to 74%.

Example 24 (comparison)

Example 21 was repeated exactly except that the 4 mmol tri-n-butylphosphine were replaced by 4 mmol tri-phenylphosphine. The conversion of olefin dropped from 64 to 29% and the percentage of terminal ester dropped from 73 to 56%.

Examples 25 to 27 (comparison)

Experiments were carried out to investigate the effects of using large quantities of triphenylphosphine. 10 ml of C₁₂ mono-olefin were used in each case. The CO pressure was 30 bar.

Example No.	Components present (mmol)	Olefin double bond position	Conversion of olefin (%)	% of terminal ester
25	0.7 Pd/P(phenyl) ₃ 9 P(phenyl) ₃	internal	6	48
26	0.7 Pd/P(phenyl) ₃ 9 P(phenyl) ₃ 0.5 g of 3%w palladium in charcoal	internal	18	42
27	0.7 Pd(CH ₃ CO ₂) ₂ 9 P(phenyl) ₃ 150 H ₂ O	terminal	4	45

Example 28 (comparison)

An experiment was carried out using a cobalt catalyst with 10 ml of a C₁₂ olefin with a terminal double bond and a CO pressure of 30 bar. The catalyst consisted of 0.7 mmol Co(CH₃CO₂)₂ and 3 mmol alpha-picoline. The conversion of olefin was high, 59%, but the percentage of terminal ester was very low, only 37%. Substantial quantities of alkane and aldehyde were formed as by-products.

Example 29 (comparison)

An experiment was carried out using a rhodium catalyst. with propene at 10 bar pressure as the olefin. and a CO pressure of 30 bar. The catalyst consisted of 0.7 mmol of $\text{Rh}(\text{CH}_3\text{COCH}_2\text{COCH}_3)_2(\text{CO})_2$ and 4 mmol tri-n-butylphosphine. The proportion of methyl butyrate amongst the products formed was only 45% molar, the remainder being largely ketones and methyl formate.

Example 30 (comparison)

0.7 g of 10%w palladium charcoal catalyst was used, along with 50 mmol acetic acid. 10 ml of internal C_{12} mono-olefin, and a CO pressure of 30 bar. However. the $\text{P}(\text{nBu})_3$ concentration was increased to 14 mmol. A high proportion of terminal ester. 65%, was produced, but the conversion of olefin dropped to only 10%.

Example 31

An experiment was carried out in which the 50 ml methanol was entirely replaced by 50 ml acetic acid. The catalyst used was 0.7 mmol palladium acetate, 4 mmol tri-n-butylphosphine. and 0.5 g of 3%w palladium on charcoal. The olefin used was propene at a pressure of 8 bar, and the CO pressure was 30 bar. A mixture of anhydrides containing n-butyryl, i-butyryl and acetyl moieties was produced at a rate of 10g/gPd/h. The ratio of n-butyryl moieties to i-butyryl moieties was 1.2:1.

Example 32

Example 31 was repeated except that the 50 ml acetic acid was replaced by 20 ml acetic acid and 25 ml sulfolane. and that 6.5 mmol tri-n-butylphosphine were used. Conversion of acetic acid to products was 35%, and the molar ratio of n-butyric acid residues to i-butyric acid residues in the product was 2:1.

Example 33

An experiment was carried out in which the 50 ml methanol was entirely replaced by a solution of 2.4 g trimethylol propane in 25 ml sulpholane as solvent. The catalyst was 0.7 mmol palladium acetate, 6.5 mmol tri-n-butylphosphine and 7 mmol propionic acid. Ethene at a pressure of 15 bar and CO at a pressure of 30 bar were introduced. After the 15 hours reaction time the reaction mixture was analysed. 86% of the alcohol had been converted to tri-ester. No mono- or di-ester was observed.

Example 34

The olefin used in this experiment was 5 ml 4-carboxybut-1-ene. the catalyst was 0.7 mmol palladium acetate and 5 mmol tri-n-butylphosphine, and the CO pressure was 30 bar. After the 15 hours reaction time. none of the olefinic acid remained in the reaction mixture. 50% molar of the product consisted of 4-methoxycarbonylbutenes. The remainder of the product was 1.4-dimethoxycarbonylbutane (70% m). 1.3-dimethoxycarbonylbutane (22% m) and 1.2-dimethoxycarbonylbutane(8% m).

Example 35

The olefin used in this experiment was 10 mls butadiene. the catalyst was 0.7 mmol palladium acetate. 4 mmol tri-n-butylphosphine, and 150 mmol water, and the CO pressure was 30 bar. Analysis of the reaction mixture showed the presence of 30% by weight of methyl 3,8-nonadienoate, plus a substantial amount of butadiene dimer.

CLAIMS

1. A process for the carbonylation of an olefin with carbon monoxide in the presence of water, an alcohol, and/or a carboxylic acid, characterized by conducting the reaction in the presence of an essentially halide-free
5 palladium catalyst and a tri-organophosphine and in the absence of sodium acetate, the tri-organophosphine containing at least one aliphatic carbon atom bound to phosphorus and the molar ratio of the organophosphine to palladium being less than 10:1.
- 10 2. A process as claimed in claim 1, characterized in that the olefin has from 2 to 30 carbon atoms and is unsubstituted or substituted by one or more of the same or different substituents selected from halogen atoms and cyano, ester, alkoxy, aryl, hydroxy and carboxy groups.
- 15 3. A process as claimed in claim 2, characterized in that the olefin is an unsubstituted alkene having one or two double bonds.
4. A process as claimed in any one of claims 1 to 3, characterized in that the olefin is carbonylated in the
20 presence of an alcohol or a carboxylic acid having up to 20 carbon atoms.
5. A process as claimed in claim 4, characterized in that the olefin is carbonylated in the presence of a mono- or poly-alkanol, an alcohol containing ether
25 linkages, or a mono- or poly-basic alkanolic acid.
6. A process as claimed in any one of claims 1 to 5, characterized in that the olefin is carbonylated in the presence of water or an alcohol, and there is added to the reaction mixture a carboxylic acid in an amount of
30 from 1 to 5 mole percent based on the number of moles of olefin.
7. A process as claimed in any one of claims 1 to 5, characterized in that the olefin is carbonylated in the

presence of an alcohol or a carboxylic acid, and there is added to the reaction mixture, water in an amount of from 1 to 5 mole percent based on the number of moles of olefin.

- 5 8. A process as claimed in any one of claims 1 to 7, characterized in that the tri-organophosphine has the general formula



in which each of R^1 and R^2 independently represents an optionally substituted alkyl, cycloalkyl or aryl group, 10 or together represent an optionally substituted alkylene group, and R^3 represents an optionally substituted alkyl or cycloalkyl group.

9. A process as claimed in claim 8, characterized in that R^3 represents an unsubstituted alkyl or cycloalkyl 15 group, an alkyl group substituted by a phenyl group, or an alkyl group substituted by a group $-\text{PR}^1\text{R}^2$, where R^1 and R^2 have the meanings given in claim 8.

10. A process as claimed in either claim 8 or claim 9, characterized in that both of R^1 and R^2 in the formula I 20 are bound to the phosphorus atom by aliphatic carbon atoms.

11. A process as claimed in any one of claims 1 to 10, characterized in that the reaction is carried out at a temperature in the range of from 100 to 200°C.



European Patent
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	GB - A - 2 014 136 (TEXACO) * Examples 1,3,4,8-12,14,22 * -----	1-5, 8-11	C 07 C 67/38 C 07 C 51/54 C 07 C 53/122 C 07 C 69/24 C 07 C 69/30 C 07 C 69/34 C 07 C 69/533 B 01 J 31/28
			TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
			C 07 C 51/00 C 07 C 53/00 C 07 C 67/00 C 07 C 69/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search VIENNA		Date of completion of the search 31-03-1982	Examiner HOFBAUER

Process for the carbonylation of olefins.

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 GB2014136 (A)

Abstract of EP 0055875 (A1)

A process for the carbonylation of an olefin with carbon monoxide in the presence of water, an alcohol, and/or a carboxylic acid, the reaction being conducted in the presence of an essentially halide-free palladium catalyst and a tri-organophosphine and in the absence of sodium acetate, the tri-organophosphine containing at least one aliphatic carbon atom bound to phosphorus and the molar ratio of the organophosphine to palladium being less than 10:1.

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